COAL/OIL COPROCESSING USING SYNGAS :REACTIVITY OF CYCLOALKANES AS THE SOLVENT.

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ABSTRACT

Coprocessing of coal or model compounds with petroleum solvents was conducted in the presence of catalysts using syngas(H_2+CO) with steam in place of hydrogen. NiMo/Al_2O_3 impregnated with potassium carbonate and NiMo/MgO catalysts exhibited good activities for hydrogenation and desulfurization. High coal conversion was obtained at a mild temperature of 400℃ for the coprocessing of coal with petroleum solvents using syngas and steam. With the solvents containing n-paraffin and cycloalkane. it was observed that decalin underwent dehydrogenation and isomerization, and that the extent of hydrodesulfurization increased with the increase of trans/cis ratio of the remaining decalin after the reaction. The presence of aromatic compounds with decalin in the solvent mixtures increased the coal conversion, suggesting that aromatic compounds could be acting as hydrogen shuttlers to transfer hydrogen from decalin to coal.

INTRODUCTION

We have reported previously[1] that coal and model compounds could be hydrogenated and desulfurized in the presence of petroleum solvents and catalyst under coprocessing conditions by using syngas with steam in place of hydrogen. Nickel molybdate on alumina support impregnated with potassium carbonate exhibited good activity with syngas and steam, presumably owing to the simultaneous water-gas shift reaction took place to form active hydrogen. We have continued our quest for catalysts that may also be active in promoting water-gas shift reaction as well as hydrotreating coal in the syngas system.
It would be more economical[2] if syngas could be used in place of expensive hydrogen in coal liquefaction or coprocessing even at the initial stage of two-stage processes.

Another aspect of this investigation is to determine the hydrogen donating ability of cycloalkanes as the solvent in coal/oil coprocessing. It appears that decalin is dehydrogenated and that hydrogen transfer to coal or model compounds takes place under coprocessing conditions. The hydrogen donating ability of decalin is enhanced in the presence of aromatic compounds.

EXPERIMENTAL

The coprocessing reactions of coal and model compounds were conducted in a shaking 25-ml microreactor with syngas (H_2:CO=1:1) or H_2 at an initial pressure of 70 kg/cm^2. The reactor was quickly heated up in a fluidizing sand bath and maintained at 400℃ for 45 minutes, and then rapidly quenched in a cold water bath. The catalysts used include a commercial NiMo/Al_2O_3 catalyst (Nippon Mining Co.) containing 12.0% MoO_3 and 2.8% NiO. a MgO supported NiMo catalyst containing 12.0% MoO_3 and 4.0% NiO. For syngas runs, the NiMo /Al_2O_3 catalyst was impregnated with 10% K_2CO_3.

Anthracene and benzothiophene were used as the model compounds, and mixtures of n-paraffin, cycloalkane, and aromatic compound were used as petroleum solvents. The ratio of solvent to model compounds was 5:1. For experiments using syngas, 10 weight % of H_2O based on the total amounts of the model compounds and solvent (roughly equivalent to H_2:CO :H_2O=1:1:0.5 in the gas phase) was added. In all runs the amount of ground catalyst powders charged was also 10 weight %.

Table 4. Product Distribution from the Resid in Binary and Ternary Systems

Reaction System	Product Distribution, wt%							
	H_2				N_2			
	HEX Solubles (%)	TOL Solubles (%)	THF Solubles (%)	IOM (%)	HEX Solubles (%)	TOL Solubles (%)	THF Solubles (%)	IOM (%)
Maya/ANT		98.8(0.2)	1.3(0.2)	0.0(0.0)		97.9(1.2)	1.8(1.2)	0.3(0.1)
Maya/ANT (Reduced)		98.2(0.2)	1.4(0.1)	0.4(0.0)		95.5(0.4)	3.6(1.1)	0.4(0.6)
DAU/ANT		96.9(0.3)	2.9(0.2)	0.2(0.1)		99.1(0.4)	0.9(0.4)	0.1(0.0)
DAU/ANT (Reduced)		96.3(0.6)	3.5(0.6)	0.2(0.1)		96.9(2.0)	2.9(2.0)	0.2(0.1)
S.LA/ANT		98.7(0.3)	1.1(0.1)	0.2(0.1)		98.2(1.1)	1.7(1.0)	0.1(0.1)
S.LA/ANT (Reduced)		98.4(0.7)	1.5(0.6)	0.2(0.1)		98.6(0.5)	1.4(0.5)	0.0(0.0)
Maya/ANT/PHP	76.8(1.2)	23.2(1.2)	0.0(0.0)	0.0(0.0)	73.7(0.9)	26.3(0.9)	0.0(0.0)	0.0(0.0)
Maya/ANT/PHP (Reduced)	78.1(2.1)	21.9(2.1)	0.0(0.0)	0.0(0.0)	81.9(0.0)	18.1(0.0)	0.0(0.0)	0.0(0.0)
DAU/ANT/PHP	81.1(1.4)	18.9(1.4)	0.0(0.0)	0.0(0.0)	76.5(0.6)	23.4(0.6)	0.0(0.0)	0.0(0.0)
DAU/ANT/PHP (Reduced)	88.4(6.1)	11.6(6.1)	0.0(0.0)	0.0(0.0)	83.0(0.3)	17.0(0.3)	0.0(0.0)	0.0(0.0)
S.LA/ANT/PHP	100.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	100.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)
S.LA/ANT/PHP (Reduced)	100.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	100.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)

DAU = deasphalted resid
S.LA = south Lousiana resid
PHP = perhydropyrene
ANT = anthracene

For coal runs, Illinois No.6 bituminous coal with an ultimate analysis of C 78.3, H 5.4, N 1.32, O 11.12, S 3.86 (maf basis), ash 10.9% and Wandan coal with C 67.5, H 5.3, N 0.9, O 15.3, ash 10.9 (mf basis) were used. The ratio of solvent to coal was 2.3:1. The coal conversion was determined from tetrahydrofuran insolubles, and the solubles were analyzed by a gas chromatograph using OV-1701 fused silica capillary column.

RESULTS AND DISCUSSION

Coprocessing Using Syngas. In general, the hydrogenation and hydrodesulfurization activities are somewhat lower with the use of syngas than with hydrogen. It is probably due to the lower partial pressure of H_2 and the existence of other components such as H_2O, CO, and CO_2 in the gas phase. Table 1 shows that the hydrogenation and hydrodesulfurization activities with $NiMo/Al_2O_3$ catalyst are somewhat reduced when the initial H_2 pressure is reduced from 70 kg/cm^2 to 35 kg/cm^2. Using syngas (without adding H_2O), we observe some decrease of hydrodesulfurization activities even at the same H_2 partial pressure of 35 kg/cm^2. With syngas, it is postulated that CO may compete with H_2 for active sites and be adsorbed on the catalyst surface. When H_2O is added, the H_2O vapor adsorbed on the surface may poison the catalyst. Therefore, it is presumably important that, for coprocessing using syngas, a suitable catalyst is used and an adequate amount of H_2O is added to promote the formation of active hydrogen via water-gas shift reaction. As was observed previously[1], the extent of the isomerization of decalin increased with the extent of hydrogenation and hydrodesulfurization. Clarke et al[3] also reported the occurence of isomerization to trans-decalin during extraction of coal using decalin as solvent.

Hydrogen Donation by Decalin. In order to find out the circumstances at which the isomerization of decalin occurs, trans-decalin and cis-decalin alone were solely hydrotreated under H_2 pressure at 400°C in the presence of $NiMo/Al_2O_3$ catalyst. The results in Table 2 show that 30.4% of cis-decalin and 7.7% of trans-decalin are isomerized, respectively. When the decalin containing both isomers at the trans/cis ratio of 1.6 was hydrotreated under the similar condition, the trans/cis ratio increased to 2.4. It is evident that decalin tends to isomerize from cis-from to trans-form under the hydroteating condition. However, in the presence of reactants (anthracene and benzothiophene), the extent of isomerization of cis-decalin solvent increased to 47.8%. On the other hand, only 7.8% of trans-decalin isomerized, indicating the difficulty for trans-decalin to isomerize to cis-form. It appears that both cis- and trans-decalin undergo dehydrogenation (to form tetralin) and hydrogen tranfer equally, but the tetralin formed probably forms trans-decalin preferentially as it is rehydrogenated. In fact, an experiment hydrotreating tetralin yielded trans-decalin preferentially (Table 2). With decalin containing both isomers as the solvent, in the presence of reactants, the trans /cis ratio after the reaction was also higher, 4.6 compared to 2.4 (see Tables 1 and 2). Coprocessing experiments using syngas with cis- and trans-decalin solvents also showed that the isomerization to trans-form was favored, but the extent of isomerization was lower.

NiMo/MgO Catalyst. In the quest for catalysts that may be active in the H_2-CO-H_2O system, a NiMo/MgO catalyst was prepared and tested. The results in Table 3 show that NiMo/MgO catalyst exhibits comparable activities with $NiMo/Al_2O_3$ catalyst for coprocessing of model compounds. In the syngas system, the alkaline MgO was able to promote CO conversion and no impregnation with K_2CO_3 was necessary. Of various catalysts tested, including synthetic pyrite, $ZnCl_2/SiO_2-Al_2O_3$, Fe_2O_3/SO_4^{2-}, cobalt molybdate, and nickel molybdate, NiMo catalysts with various characteristics of supports may be the most interesting area to explore.

Coprocessing of Coal with Petroleum Solvents. Table 4 shows the experimental results of coprocessing Illinois No.6 coal and Wandoan coal with petroleum solvents. At the mild temperature of 400°C, $NiMo/Al_2O_3$ catalyst impregnated with K_2CO_3 exhibited good activities with syngas, and high coal conversions obtained were comparable to those obtained with hydrogen. At temperatures greater than 425°C, because of lower H_2 partial

pressures with syngas, the fragments from thermally decomposed coal tend to polymerize to form char. The experimental runs using NiMo/MgO catalysts show that coal conversions were somewhat lower with either H_2 or syngas.

It was also observed that hydrogen donating properties of paraffin-cycloalkane solvent mixtures were enhanced by the presence of cyclic compounds containing benzene rings such as tetralin and 1-methylnaphthalene. Even though 1-methylnaphthalene is not a hydrogen donor, its addition to the dodecane-decalin mixture increased the coal conversion, equivalent to that obtained with the addition of tetralin (see Table 4). This suggests that aromatic compounds, in paraffin-cycloalkane solvents, may act as hydrogen shuttlers to transfer hydrogen from cycloalkane to coal.

References

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Table 1 Coprocessing of Model Compounds with Petroleum Solvents
(Catalyst:NiMo/Al₂O₃, Reaction temp.:400℃, Time:45min)

Gas	H₂	H₂	Syngas	Syngas+H₂O[a]
Initial pressure kg/cm²	70	35	70	70
Solvent[b]	DO/DL	DO/DL	DO/DL	DO/DL[c]
Anthracene conv.,%	89.4	65.3	63.1	90.6
Benzothiophene conv.,%	100	80.0	71.6	52.6
Decalin remained.%	76.2	66.5	88.5	75.3
cis	13.7	15.5	62.5	47.0
trans	62.5	51.0	26.0	28.3
trans/cis ratio	4.6	3.3	2.4	0.6
CO conv.,%	-	-	13.1	35.2

DO:Dodecane, DL:Decalin

a) NiMo/Al₂O₃ impregnated with K₂CO₃

b) Equal wt% of each component

c) 100% cis-Decalin

Table 2 Coprocessing Using Decalin Isomers as Solvents
(Initial Pressure:70 kg/cm², Temperature:400℃, Time:45min)

Gas	H₂						Syngas+H₂O	
Catalyst	NiMo/Al₂O₃						NiMo-K₂CO₃/Al₂O₃	
Solvent	c-DL	DO/c-DL	t-DL	DO/t-DL	DO/DL	T	DO/c-DL	DO/t-DL
Model compound	-	A,B	-	A,B	-	-	A,B	A,B
A conv.,%	-	98.5	-	98.9	-	-	90.6	83.0
B conv.,%	-	94.9	-	94.3	-	-	52.6	46.5
EB formed.%	-	69.3	-	62.8	-	-	19.1	23.5
Decalin remained.%	96.1[a]	94.7	98.9[a]	82.3	92.4	11.0[b]	75.3	87.0
cis	65.7	46.9	7.7	7.8	27.4	2.8	47.0	6.4
trans	30.4	47.8	91.2	74.5	65.0	8.2	28.3	80.5
trans/cis ratio	0.46	1.0	11.8	9.6	2.4	2.9	0.6	12.5
CO conv.,%	-	-	-	-	-	-	35.2	28.7

c-DL:cis-Decalin, t-DL:trans-Decalin, DO:Dodecane, T:Tetralin

A:Anthracene, B:Benzothiophene, EB:Ethylbenzene

a) The remainder converted to tetralin.

b) Decalin formed. Tetralin remained is 84.2%, and the remainder converted to naphthalene.

Table 3　Coprocessing of Model Compounds on NiMo Catalysts
　　　　　(Solvent:n-Decane/Decalin/Tetralin, Initial Pressure:70 kg/cm²,
　　　　　Temp.:400℃, Time:45min)

Catalyst	H₂		Syngas+H₂O	
	NiMo/Al₂O₃	NiMo/MgO	NiMo/Al₂O₃[a]	NiMo/MgO
Anthracene conv.,%	100	100	96.1	99.2
Benzothiophene conv.,%	100	100	93.9	100
Ethylbenzene formed,%	80.5	78.8	83.7	88.3
H₂ consumption,%[b]	7.0	5.1	0.3	-0.5
CO conv.,%	-	-	37.2	40.6
Decalin remaind,%	116.4	85.5	92.5	96.3
cis	27.2	24.5	26.7	27.3
trans	89.2	61.0	65.8	69.0
trans/cis ratio	3.3	2.5	2.5	2.5
Tetralin conv.,%	34.4	24.4	12.2	19.0
Naphthalene formed,%[c]	6.8	3.8	4.1	9.3

a) Impregnated with K₂CO₃
b) Wt.% of coal models
c) Based on the initial amount of tetralin

Table 4　Coprocessing of Coals with Petroleum Solvents at 400℃

Gas	H₂				Syngas(H₂:CO=1:1)			
Catalyst	NiMo/Al₂O₃			NiMo/MgO	NiMo/Al₂O₃[a]			NiMo/MgO
Solvent	DO/DL/T	DO/DL/MN	D/DL/T	D/DL/T	DO/DL/T	DO/DL/MN	D/DL/T	D/DL/T
Coal conversion,%	89.0[b]	86.5[b]	89.9[c]	76.7[c]	87.9[b]	85.5[b]	87.3[c]	74.8[c]
H₂ consumption,wt% of maf coal	3.9	4.5	5.5	2.3	0.9	0.9	-1.3	-0.2
CO conv.,%	-	-	-	-	7.3	12.0	46.0	28.5
Decalin remained,%	98.1	89.9	88.4	96.6	95.8	94.3	85.3	97.9
cis	33.7	29.8	33.7	36.5	33.3	34.5	31.9	36.9
trans	64.4	60.1	54.7	60.1	62.5	59.8	53.4	61.0
trans/cis ratio	1.9	2.0	1.6	1.6	1.9	1.7	1.7	1.7
Tetralin conv.,%	2.3	10.3[d]	3.5	0.3	11.1	7.7[d]	17.1	1.0

D:n-Decane, DO:Dodecane, DL:Decalin, T:Tetralin, MN:1-Methylnaphthalene
a) Impregnated with K₂CO₃ solution
b) Illinois No.6 coal
c) Wandoan coal
d) Conversion of 1-Methylnaphthalene